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Research paper

Classification of Oil Palm Fresh Fruit Bunches (FFB) Using Raman Spectroscopy

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Abstract

The current practice in determining oil palm fresh fruit bunches (FFB) ripeness is by its colour which could be inaccurate. This study investigates the classification of oil palm FFB ripeness using Raman spectroscopy. A feature extraction model is developed based on the different organic compositions that contribute to the ripeness classification. Samples are collected according to the Malaysian Palm Oil Board (MPOB) standards which are unripe, underripe, ripe, overripe, and rotten. Different characteristics of the Raman shift were detected which represent the material composition for each sample. The Raman intensity of the oil palm fruit increases from unripe to ripe before decreasing to rotten due to the carotenoid content in the fruit. In conclusion, Raman spectroscopy is a suitable technique to observe the changes in the composition of oil palm fruit classified by its ripeness.

Keywords: *oil palm fruit; Raman spectroscopy; ripeness; carotenoids.*

1. Introduction

Palm oil (Elaeis guineensis) production is very crucial for the Malaysian economy as the world's second largest producer right after Indonesia. Palm oil trees were introduced to Malaysia in early 1870s, and today, the palm oil industry has expanded the export market to over 140 countries [1].

As the largest exporters of palm oil in the world, Malaysia certainly has its own technology and formula to produce quality palm oil [2]. The development in food trade has significantly changed the way food is produced and consumed [3], no matter if it is based on palm fruit or not. Existing technologies have improved product yields and enabled trade to be extended across borders especially between Malaysia and other countries. The market potential for food oils and fats remains good into the future considering the increases in population, income and per capita consumption. Palm oil is the second most produced vegetable oil after soybean oil and the most traded vegetable oil in the world [4]. Research studies are more towards the ways of planting, harvesting, palm oil care and medicinal purposes [5]. The oil palm fruit must be accurately selected for oil production that will be used for medical purpose. Therefore, the determination of ripeness of palm oil fruit is very important to obtain the best quality of crop yield.

Among the studies conducted to determine the ripeness of oil palm fruits are using computer vision [6], hyperspectral imaging [7], visible-near infrared (VIS/NIR) spectroscopy [8], fluorescence sensing [9], capacitive sensing [10], and inductive sensing [11-13]. The computer vision method has low cost as it only uses digital cameras. However, captured images are often influenced by the sun's intensity and thus not suitable for use under different light intensity. Hyperspectral imaging method is better than visual computer and can provide a lot of information but its high cost devices are the major obstacle. Inductive and capacitive sensing methods are not suitable for site grading as they are developed for use with automatic grading machines in factories. Farmers are still relying on eyesight to determine the ripeness up to these days. One of the most common techniques is by observing the colour and quantity of fallen ripe oil palm fruitlets near the tree. When there are more than 5 palm fruitlets under a tree, it indicates that the bunch is ready to be harvested. The mentioned standard for classifying the ripeness has been established by Thailand department of agriculture [14], Indonesian Oil Palm Research Institute (IOPRI) and Malaysian Palm Oil Board (MPOB) [15].

Another method for determination of ripeness of palm oil fruit is spectroscopy sensing. Spectroscopy measures the interaction of light with matter. Light is composed of electromagnetic vectors that freely rotate as it propagates under normal circumstances. When light strikes matter, the interactions could be observed through spectroscopy. Raman spectroscopy is a technique to study the vibrational characteristics of molecules when a laser light source is used to illuminate a sample. Raman scattering occurs when a photon interacts with functional groups of the sample molecules. When using a high-powered laser as the light source, the object of interest could be placed further away than using close proximity spectroscopy. Therefore, Raman spectroscopy is a promising method and tool to determine the ripeness of oil palm fruit. Raman spectroscopy is used frequently to analyze and identify the component make-up of a sample in many fields of study. Several studies for molecular or component detection conducted before include measurements on tomato ripeness [16] and citrus fruit freshness [17]. In this work, the aim is to identify and evaluate different organic compositions that contribute to the ripeness classification, and to develop a features extraction model for ripeness classification using the organic characteristic data collected in a controlled environment using Raman spectroscope.

2. Methodology

2.1. Samples

This work gives focus on the oil palm fresh fruit bunches (FFB) obtained from the National University of Malaysia (UKM) palm oil plantation supervised by Khazanah UKM. There are 3 types of oil palm fruit according to its shell: Elaeis guineensis fo. dura (oil palm fruit with thick shell), Elaeis guineensis var. tenera (oil palm fruit with thin shell), and Elaeis guineensis fo. pisifera (oil palm fruit without shell). The samples collected are from Elaeis guineensis DxP oil palm fruit, which is the hybrid of the dura and pisifera species. This hybrid palm tree has short and big appearance and is generally known as DxP oil palm fruit species.

The sample collected is categorized according to the ripeness category set by the Malaysian Palm Oil Board (MPOB). According to [15], it is stated that purplish black as unripe, reddish black as underripe, red as ripe, reddish orange as overripe, and dried, black, and moldy as rotten. The samples are collected in the morning to avoid any sun exposure that could affect the fruit. It is also to maintain the same temperature of collected samples to be constant throughout the study.

The example on how to cut the oil palm fruit into slices is shown in Fig. 1(a) and the actual sliced oil palm fruit is shown in Fig. 1(b). The samples are prepared by cutting its skin into slices from the top to bottom part of the fruitlet for spectroscopy scanning. The skins of the samples are cut 120° apart from each other to test the difference between each side of the fruitlet that is 120° apart from each other. It is expected to have no changes between them and thus lead to next sample preparation, which is preparing the skin slices from the top to bottom part of the fruitlet. The scanning was done for the top, middle and bottom part of the sliced skin. It is expected that there are significant differences between these parts. Finally, a sample of sliced skin of each category of ripeness is prepared to observe the organic changes in each sample.

(a) (b)

Fig. 1: (a) Example of orange fruit sliced from top to the bottom part and, (b) the sliced oil palm fruit

2.2. Instrumentation

Raman measurements of the unripe, underripe, ripe, overripe, and rotten oil palm fruitlets were carried out using Thermo Scientific™ DXR™2xi Raman imaging microscope that allows polarized point measurements to be performed on submicron spatial resolution over large areas. For this work, 532 nm NIR laser is used. The laser power was controlled in order to avoid possible thermal decomposition of carotenoids and further organic compounds of oil palm fruits.

The samples are treated with care as to not put any stress on it that could cause structural damage. If stress was applied to the samples, the Raman shift or wavenumber could be altered. The 532 nm NIR laser is directed to the skin of oil palm fruit that had been sliced earlier to obtain the microscopic view. A suitable area is then selected to perform the point measurements or also known as spot scanning. The spectroscope will calculate and find the mean values for the area chosen to give the output spectrum consisting of Raman intensity and wavenumber. The measurements were conducted with fruitlets to identify the percentage of ripeness of a bunch.

3. Results and Discussion

From Raman measurements performed on all the samples for this work, there are several notable wavenumber or Raman shift obtained. In [16] mentioned that the wavenumber at 870 cm^{-1}, 949 cm^{-1}, 999 cm^{-1}, 1007 cm^{-1}, 1149 cm^{-1}, 1184 cm^{-1}, 1209 cm^{-1}, 1269 cm^{-1}, 1277 cm^{-1}, 1310 cm^{-1}, 1510 cm^{-1}, 1524 cm^{-1} and 1553 cm^{-1} are all identified as chemical compound that came from the carotenoid family. He also mentioned that the bands around 1002 cm^{-1} and 1524 cm^{-1} are the key wavenumbers to determinate that the lutein is the principal carotenoid. The wavenumber at 870 cm^{-1}, 1007 cm^{-1}, 1184 cm^{-1}, 1209 cm^{-1}, 1277 cm^{-1} and 1510 cm^{-1} falls under the additional carotenoid that is related to carotenes. In [18] also mentioned that wavenumber at 1269 cm^{-1} and 1310 cm^{-1} are the main contributor to β-carotene. However, in the Raman spectra obtained, it is very difficult to identify these wavenumbers as the intensity is almost the same as other wavenumbers. Although the wavenumber at 1553 cm^{-1} could be identified and represented as either phytoene or phytofluene, the peak intensity at that particular wavenumber does not give a high value for it to be taken and considered as notable data. A similar behavior to identify the meaning of wavenumber at 1553 cm^{-1} had been observed by [16]. Therefore, it could be concluded that there are five significant peaks that show the molecular vibrational assignments that contribute to the ripening process of oil palm fruit. The identified peaks are 949 cm^{-1}, 999 cm^{-1}, 1149 cm^{-1}, 1277 cm^{-1}, and 1510 cm^{-1}. All of these peaks are related to carotenoid and thus changes of the intensity data will correspond to changes of carotenoid content in the oil palm fruit.

Since there is no abundant data on wavenumber or Raman shift that could be relied on to determine the ripeness level of oil palm fruit, thus the changes of intensity data is used. The first set of Raman measurements were performed with three samples that were taken from the sides, which are the front, left and right of oil palm fruit. Table 1 show the assignments (cm^{-1}) of vibrational modes identified in the spectra of front, left, and right side of oil palm fruits obtained with Raman spectroscopy using 532 nm laser excitation wavelength. The spectra obtained on the surface of the oil palm fruit of all three sides are all the same and they almost overlapped when put on top of each other as shown in Fig. 2. The significant peaks located at 949 cm^{-1}, 999 cm^{-1}, 1149 cm^{-1}, 1277 cm^{-1}, and 1510 cm^{-1} are identified at each side of the oil palm fruit. This proves that at any angle of perspective when looking at the oil palm fruit whether it is from the front, left or the right side, the level of ripeness would not be affected as all three sides show the same data as obtained from Raman scanning. The reason for the data obtained to be the same could be due to the ripening process that happens evenly for all three sides throughout the fruit.

Table 1: Assignments (cm^{-1}) of vibrational modes identified in the spectra of front, left, and right side of oil palm fruits obtained with Raman spectroscopy using 532 nm laser excitation wavelength.

Front Side	Left Side	Right Side	Molecular Assignment
949	949	949	Carotene (CH_3)
997	997	997	Carotene (C—CH_3)
1149	1149	1149	Carotene (C—C)
1275	1275	1275	Carotene (=C—H)
1510	1510	1510	Carotene (C=C)

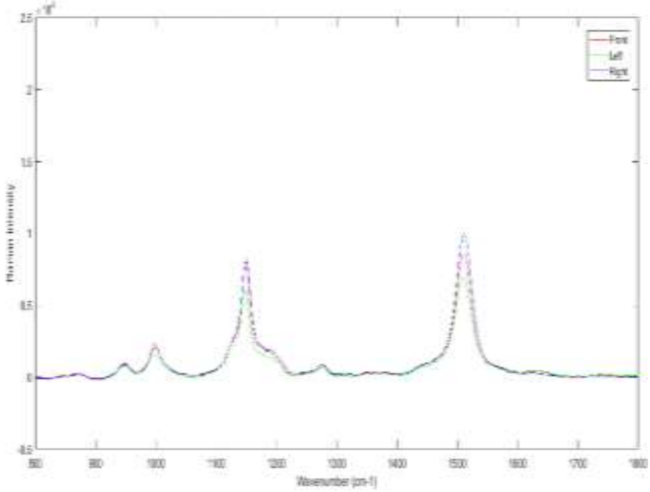

Fig. 2: Raman spectra of oil palm fruit at three different sides obtained with Raman spectrometer

After knowing that there are no changes for the three sides of the oil palm fruit, the second set of Raman measurements were performed with a sample, which are the top, middle and bottom part of the sliced oil palm fruit. Table 2 shows the assignments (cm^{-1}) of vibrational modes identified in the spectra of top, middle, and bottom part of the oil palm fruits obtained with Raman spectroscopy using 532 nm laser excitation wavelength. The spectra obtained on the surface of the oil palm fruit of all three parts have different values of intensity as shown in Fig. 3. The significant peaks located at 949 cm^{-1}, 999 cm^{-1}, 1149 cm^{-1}, 1277 cm^{-1}, and 1510 cm^{-1} are identified at each part of a slice of an oil palm fruit. The intensity data of Raman spectra gives information about the quantity of a specific compound at a particular wavenumber. From the spectra, it is identified that the top part of the oil palm fruit gives the highest Raman intensity compared to others. This is believed due to the amount of sunlight the palm tree was exposed to. Since the top is outwardly facing, it has more syntheses frequencies which helps ripen the top part faster than the rest of the fruitlet.

Table 2: Assignments (cm^{-1}) of vibrational modes identified in the spectra of top, middle, and bottom part of oil palm fruits obtained with Raman spectroscopy using 532 nm laser excitation wavelength.

Top Part	Middle Part	Bottom Part	Molecular Assignment
949	949	949	Carotene (CH3)
999	999	999	Carotene (C—CH3)
1149	1149	1149	Carotene (C—C)
1277	1277	1277	Carotene (═C—H)
1512	1512	1512	Carotene (C═C)

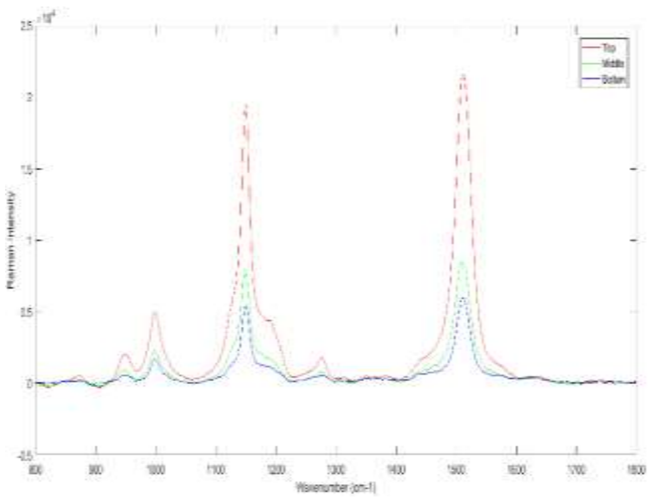

Fig. 3: Raman spectra of oil palm fruit at three different parts obtained with the Raman spectrometer

The third set of Raman measurements were performed for five different ripening stages which are unripe, underripe, ripe, overripe and rotten oil palm fruits. Table 3 shows the assignments (cm^{-1}) of vibrational modes identified in the spectra of unripe, underripe, ripe, overripe, and rotten oil palm fruits obtained with Raman spectroscopy using 532 nm laser excitation wavelength. The spectra obtained on the surface of the oil palm fruit of all five ripeness have different values of intensity as shown in Fig. 4. The significant peaks located at 949 cm^{-1}, 999 cm^{-1}, 1149 cm^{-1}, 1277 cm^{-1}, and 1510 cm^{-1} are identified at each ripeness stage of oil palm fruit. From the spectra, it is identified that ripe fruit gives the highest Raman intensity compared to other ripeness stages. The trend of ripening process for oil palm fruit is increasing from the unripe to ripe stage, and then decreasing until the rotten stage. It is believed that this happens because ripening is a process that changes for each stage at that particular time. The internal compound syntheses will increase inversely with the Raman intensity. The declining value of intensity after the oil palm fruit passes the harvesting period of the ripe stage is due to the fact that carotene will disintegrate to other chemical compounds after the ripe stage.

Table 3: Assignments (cm^{-1}) of vibrational modes identified in the spectra of unripe, underripe, ripe, overripe, and rotten oil palm fruits obtained with Raman spectroscopy using 532 nm laser excitation wavelength.

Unripe Fruit	Underripe Fruit	Ripe Fruit	Overripe Fruit	Rotten Fruit	Molecular Assignment
951	951	951	951	951	Carotene (CH3)
999	999	999	999	999	Carotene (C—CH3)
1149	1149	1149	1149	1149	Carotene (C—C)
1275	1275	1275	1275	1275	Carotene (═C—H)
1510	1510	1510	1510	1510	Carotene (C═C)

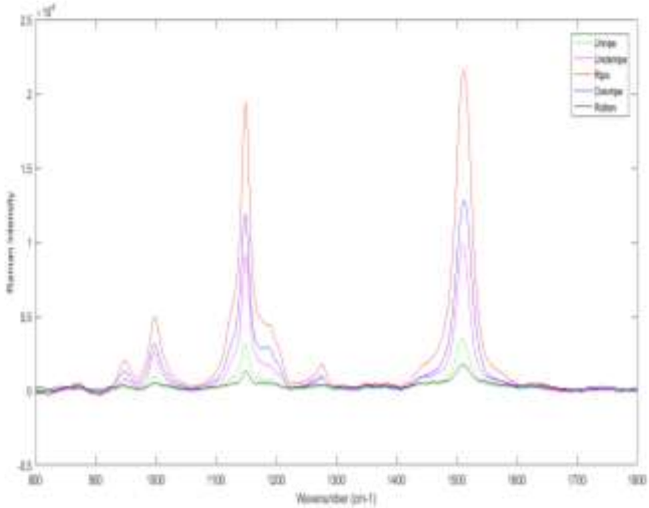

Fig. 4: Raman spectra of oil palm fruit at five different ripening stages obtained with the Raman microscope with the Raman spectrometer

Other than observing the intensity data with respect to its wavenumber, the full width at half maximum (FWHM) is also calculated. FWHM is the width of a peak at half of its intensity and it indicates the changes in crystallinity or the molecular composition. It is known that the smaller the size, the greater the value of FWHM. The result as in Fig. 5 shows that the FWHM is very high at ripe stage as carotenoid is the prime organic characteristic. The trend of the FWHM analysis performed is almost the same value for unripe and underripe stage, increasing towards the ripe stage before decreasing towards the rotten stage. This is due to the ripening process where internal syntheses will occur more at the ripe stage and thus more carotenoid quantity is found during that period.

The ratio between two significant peaks are calculated and shown in Fig. 6. One of the reasons to analyse the data ratio is to determine if the intensity data with respect to wavenumber is significant enough to be observed for future work. The trend of peak ratio is also a good indicator to guide future work for classification. The peak ratio between peak 5 (1510 cm^{-1}) to peak 2 (999 cm^{-1}) is the best among other peak ratios throughout the ripening process due to its bell-shaped trend. The peak ratio between peak 5 to peak 3 (1149 cm^{-1}) does not show any changes throughout the ripening process which makes the data between peak 5 and peak 3 not significant enough to be compared together.

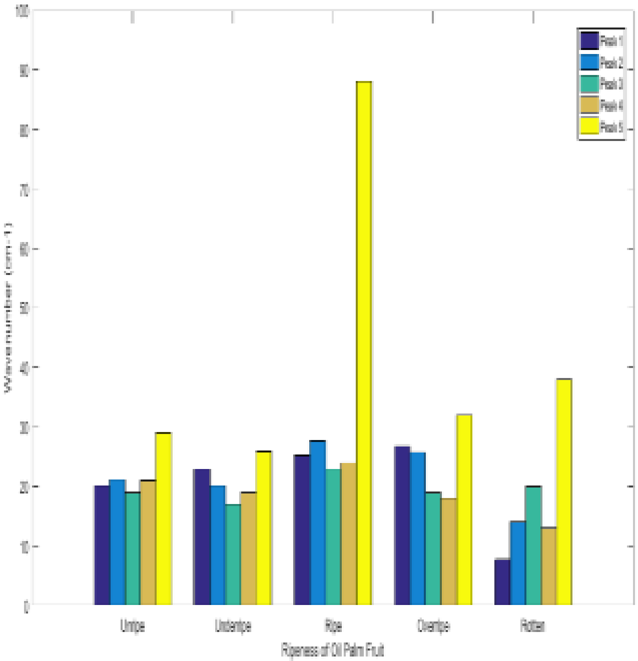

Fig. 5: FWHM of five significant peaks from Raman spectra of oil palm fruit at five different ripening stages obtained with the Raman spectrometer

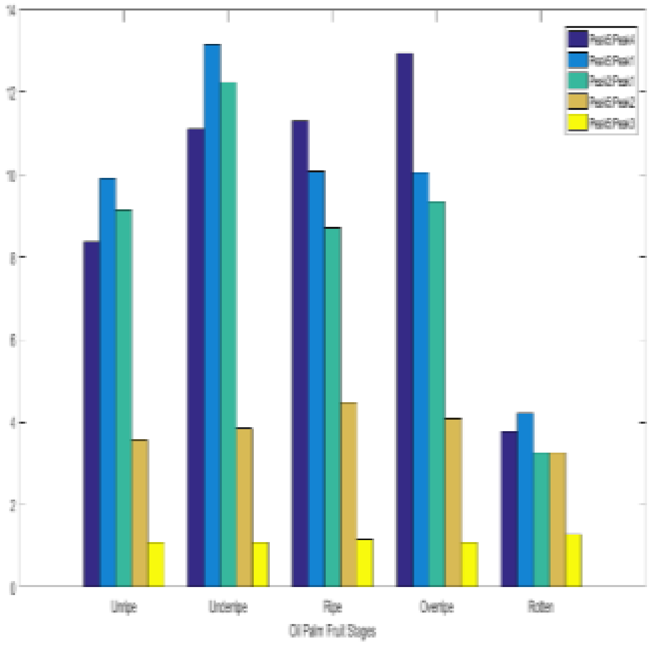

Fig. 6: Ratio between two peaks from Raman spectra of oil palm fruit at five different ripening stages obtained with the Raman spectrometer

4. Conclusion

Raman spectroscopy is a suitable technique to observe the changes of organic composition of oil palm fruit that is contrasted by the appearance of the skin color of the fruit. Raman spectroscopy distinguishes all the vibrational modes related with key compounds useful to monitor the ripening stage of oil palm fruit. It gives a valuable data to observe the ripeness of oil palm FFB according to its intensity of organic composition. As the increase or decrease in intensity caused by the different organic compositions present in oil palm fruits are observed, it shows that Raman spectroscopy gives significant data for observing and determining the ripeness of oil palm FFB. It also provides sensitive and fast observation that could prevent possible blackened and molding of oil palm fruit as it passes the ripe stage when it should be harvested. With this technique, crop collection would be easier and the palm oil market industry could profit more out of it.

It is found that carotenoid is the dominant organic composition extracted from Raman spectrum to determine the ripeness in oil palm fruit. In addition to providing a method in evaluating the ripening process, Raman spectroscopy can also offer valuable information about the organic molecules associated with each ripening stage.

The results obtained from this research are useful to develop an artificial neural network (ANN) model by obtaining a large number of samples of oil palm fruits to be scanned. Furthermore, the results obtained could also be benefited for the design of a portable Raman spectroscope. This spectroscope would not have the same function as the one used in the laboratory for this work, which scans the whole wavenumber or Raman shift that is from 800 to 1800 cm^{-1}. Rather, it will consist of a single wavelength of 532 nm that will cover wavenumbers from 1000 to 1500 cm^{-1}. From there, the different value of intensities will determine the ripeness level of the oil palm fruit.

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